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THE VOLATILE ACIDITY OF GUM TRAGACANTH COMPARED WITH THAT OF INDIAN GUM.

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NEED OF THE INVESTIGATION.

The primary object of this investigation was to devise additional methods for the detection of Indian gum when substituted for or in admixture with tragacanth. A study of the literature early led to the conviction that among the degradation products of these gums there must be one susceptible of quantitative isolation and sufficiently characteristic to serve as an indicator of the purity, and therefore of the quantity, of parent substance involved in its hydrolysis. Such an indicator was believed to be represented by acetic acid, already isolated from one Indian gum and reported as being present in another. The hope was entertained that tragacanth under like treatment might fail to yield this acid, but as will presently appear, experiment proved otherwise.

As defined by the United States Pharmacopœia, tragacanth is the "gummy exudation from *Astragalus gummifer* Labillardière, or from other species of Astragalus, family Leguminosæ, appearing in ribbon-shaped bands varying in size and from 1 to 3 mm thick, or in irregular pieces of the same, long and linear, straight or spirally twisted; externally whitish, marked by more or less pronounced longitudinal or eccentric lines or ridges; translucent, fracture, short, tough, rendered more easily pulverizable by a heat of 50° C. (122° F.)."

While it is possible that the products known to the trade as "Indian gum" and employed so extensively in this country may vary as to their origin, it appears reasonably certain that two gums at least are justly characterized by this term, namely those of *Sterculia urens* and *Cochlospermum gossypium*, both of which find local application as substitutes for tragacanth. It is equally certain that none of the so-called Indian gum has its origin in any species of Astragalus. Most of the Indian gum reaching this country bears little

or no resemblance to tragacanth. A careful comparison of the commodity with authentic samples obtained direct, both from London and from India, clearly indicates that it corresponds in all essential points to the gum of *Sterculia urens*. It occurs in irregular, striated, sometimes twisted, translucent, or transparent lumps, never in ribbon-shaped bands or leaves.

In view of such physical characteristics, successful adulteration or substitution of whole gum tragacanth with Indian gum is no easy matter, and yet the latter product is occasionally offered for sale in the bazaars of India as true tragacanth.[1] It is, however, the powdered form of tragacanth that presents to the sophisticator more alluring possibilities. Owing to its extended use in the arts as well as in medicine, coupled with a relatively high price for the better grades, adulteration with the cheaper Indian gum has within the past few years been of frequent occurrence, hence any method looking to the detection and estimation of such adulterant must be welcome to all desirous of obtaining pure powdered tragacanth.

CHEMICAL PROPERTIES OF GUM TRAGACANTH.

According to researches carried on by O'Sullivan[2] tragacanth consists of starch granules, cellulose—that portion insoluble in boiling water, cold dilute acids, and alkalies—likewise water-soluble gum yielding a series of gum acids of the nature of geddic acid, bassorin, bassoric acid, nitrogenous and mineral matter. As the result of an investigation of tragacanth from various sources, Hilger and Dreyfus,[3] among other conclusions, found that this product differs not only as regards chemical constitution, but also with respect to the proportion of degradation products formed when subjected to hydrolysis. None of the investigators of tragacanth, however, has, to the writer's knowledge, ever considered the possibility of acetic or other volatile acid constituting one of the hydrolytic products of this gum, due perhaps to the fact that it is odorless and without acid reaction in aqueous suspension, conditions not obtaining in the case of the two Indian gums herein considered. The remarkable property possessed by the gums of *Sterculia urens* and *Cochlospermum gossypium* of developing an acetous odor when exposed to moist air has been commented on by various authors; in fact, an examination by Robinson[4] of the hydrolytic products obtained with the gum of *Cochlospermum gossypium* developed the fact that an amount of acetic acid was formed equivalent to 14.4 per cent of the original gum.

[1] Zörnig, Arzneidrogen, 1909, p. 654.
[2] J. Chem. Soc., Trans., 1901, *79:* 1164; Proc. 1901, p. 156.
[3] Ber. d. chem. Ges., 1900, *33:* 1190.
[4] J. Chem. Soc., Trans., 1906, *89:* 1496.

When gum tragacanth is heated with an aqueous mineral acid, as phosphoric or sulphuric acids, and the products of such action subjected to steam distillation, an acid distillate is obtained from which acetic acid can readily be isolated in the form of its silver salt. The procedure employed is as follows:

Treat 20 grams of whole gum first in the cold with 200 cc of distilled water and 10 cc of sirupy phosphoric acid until completely swollen, then subject for several hours to the full heat of the steam bath, whereby the mass gradually becomes partially liquefied, then distill the product with steam and evaporate the distillate to dryness in the presence of barium carbonate. Treat the residue with a little hot water, filter, and distill the filtrate, amounting to about 30 cc, with steam after the addition of 5 cc of sirupy phosphoric acid.

On treating the distillate with silver oxid and filtering, characteristic plate-like needles are obtained, which on ignition prove to be silver acetate, as is evidenced by the following analytical data: 0.2048 gram of substance gave 0.1321 gram of silver; calculation for $C_2H_3O_2Ag$ gave 64.65 per cent of silver, 64.50 per cent being found.

There can, therefore, be no doubt that acetic acid constitutes one of the degradation products of tragacanth when heated with mineral acids.

ESTIMATION OF ACETIC ACID.

Quantitatively, the acetic acid or, rather, "volatile acidity" [1] is estimated as follows:

Treat 1 gram of the whole or powdered sample in a 700 cc round-bottomed flask, provided with a long neck, for several hours in the cold with 100 cc of distilled water and 5 cc of sirupy phosphoric acid until the gum is completely swollen. Boil gently two hours in connection with a reflux condenser, whereby a nearly clear, colorless solution is effected. A very small amount of cellulose substance will remain undissolved. Now subject the hydrolyzed product to slow distillation in a vigorous current of steam until the distillate amounts to 600 cc and the acid residue to about 20 cc. This should not be driven too far, however, otherwise there may be danger of scorching the nonvolatile, organic degradation products, with consequent possible contamination of the distillate. It has been found that a spray trap of the form shown in figure 1, if used in connection with the flask containing the hydrolyzed gum, is effective in preventing traces of phosphoric acid being carried over into the distillate. Titrate with tenth-normal potassium hydroxid in connection with 10 drops of phenolphthalein solution, finally boiling the liquid under examination until a faint pink color persists. Run a control on same amount of distillate obtained by a parallel operation, with omission of gum, but using like quantities of other ingredients and observing the same conditions as in the test.

With a relatively large number of authentic gums (Turkey, Aleppo, and Persian), both whole and powdered, the following results were obtained:

Results on 35 samples of gum tragacanth lump (cubic centimeters of tenth-normal potassium hydroxid): 3.9, 3.5, 4.2, 4.0, 3.4, 4.0,

[1] The term "volatile acidity" as used herein is the number of cubic centimeters of tenth-normal potassium hydroxid required to neutralize the volatile acid or acids obtained, by subjecting the products of the action of aqueous phosphoric acid on 1 gram of gum to distillation with steam.

3.2, 3.5, 4.0, 3.9, 3.4, 3.4, 3.6, 3.4, 3.5, 4.2, 4.0, 3.6, 3.3, 3.6, 3.8, 3.4, 3.3, 3.6, 3.4, 3.1, 3.3, 3.5, 3.4, 3.7, 3.4, 3.7, 3.7, 3.2, 3.4. These figures represent an average volatile acidity of 3.6 cc. Assuming this acidity to be due solely to acetic acid, it would be equivalent to 2.15 per cent of acetic acid in the original gum.

Results on 21 samples of gum tragacanth powdered (cc tenth-normal potassium hydroxid): 3.8, 3.5, 3.5, 3.5, 3.6, 4.1, 3.8, 3.4, 3.9, 3.9, 3.5, 3.7, 3.8, 3.9, 3.6, 3.8, 3.6, 3.8, 3.5, 3.6, 3.8. This gives an average volatile acidity of 3.7 cc, equivalent to 2.20 per cent of acetic acid in the original gum.

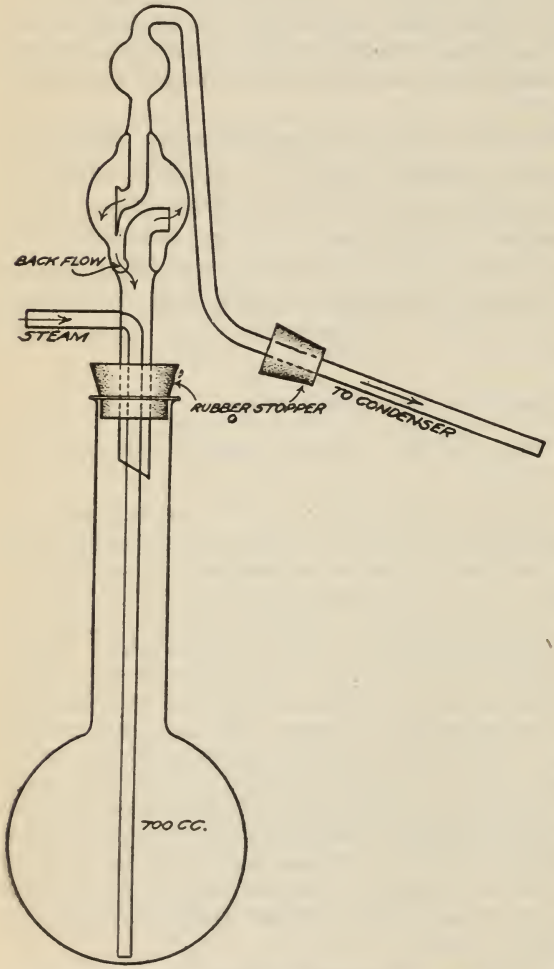

FIG. 1.—Spray trap for distillation of volatile acids.

As regards the acetic acid content of Indian gum (*Cochlospermum gossypium*) it has already been shown by Robinson[1] to yield 14.4 per cent of this acid. That of *Sterculia urens*, however, though early recorded by Guibourt[2] as emitting an acetous odor, has never before to the writer's knowledge been examined either as to the identity or the quantity of the acetic acid present. Five grams of Indian gum (*Sterculia urens*) were therefore treated in substantially the same manner as outlined for the isolation of the silver salt from the hydrolytic products of tragacanth. It may not be amiss to note in this connection that while tragacanth yields a practically colorless solution when boiled with aqueous phosphoric acid, Indian gum, on the other hand, gives a pink or rose colored solution, a sure indication in an unknown sample that this product is present.

[1] Loc. cit.

[2] Pharm. J., 1855, *15*: 57.

The acid distillate obtained gave with silver oxid characteristic plate-like needles, which on ignition yielded values corresponding to silver acetate: 0.2010 gram of substance gave 0.1300 gram of silver, calculation for $C_2H_3O_2Ag$ gave 64.65 per cent, 64.67 per cent being found.

Gram samples of whole and powdered Indian gum (*Sterculia urens*) were examined for volatile acidity, exactly as in the case of tragacanth, with the following results:

Results on 9 samples of Indian gum, lump (cc tenth-normal potassium hydroxid): 26.3, 26.1, 26.6, 27.7, 27.1, 28.3, 25.9, 26.1, 26.8. These data indicate an average volatile acidity of 26.7 cc, corresponding to 15.91 per cent of acetic acid in the original gum. The last of the nine samples, yielding 26.8 cc, was an authentic one obtained direct from the Indian Government; this acidity corresponds to 15.97 per cent acetic acid.

Results of 14 samples of Indian gum, powdered (cc tenth-normal potassium hydroxid): 26.5, 26.3, 26.1, 27.3, 26.3, 26.9, 25.4, 25.6, 27.7, 26.8, 26.6, 25.6, 27.6, 26.0. The average volatile acidity in this case is 26.5 cc, corresponding to 15.79 per cent of acetic acid.

CONCLUSIONS.

From the foregoing data it appears that the volatile acidity or amount of volatile acid developed by gram samples of tragacanth, on the one hand, and Indian gum (*Sterculia urens*), on the other, is fairly constant, sufficiently so, indeed, to serve, in conjunction with other well-known tests, as a very reliable criterion for estimating the purity or quantity of either alone or in admixture. The volatile acidity of Indian gum (*Sterculia urens*) as compared with that of tragacanth is nearly 7.5 times as great.

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